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**Wagaman**

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(54) **GAS-GENERATING LIQUID  
COMPOSITIONS (PERSOL 2)**

5,703,323 12/1997 Rothgery et al. 149/88

**OTHER PUBLICATIONS**

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(58) **Field of Search** **149/45, 46, 109/6**

(56) **References Cited**

**U.S. PATENT DOCUMENTS**

H1768	1/1999	Mueller et al.	
3,145,082 *	8/1964	Rausch et al.	423/275
3,561,533	2/1971	McKinnell	
3,790,415	2/1974	Tomic	
3,923,565 *	12/1975	Sakai et al.	149/60
4,047,988	9/1977	Weill et al.	
4,507,161 *	3/1985	Sujansky et al.	149/21
5,223,057 *	6/1993	Mueller et al.	149/45
5,607,181	3/1997	Richardson et al.	

Anderson, W., et al. Low-Cost Propulsion Using a High-Density, Storable, and Clean Propellant Combination. Mul. et al. Search for New Storable high Performance Propellants, (AIAA-88-3354, AIAA/ASME/SAE/ASEE 24th Joint Propulsion Conference, Boston, Jul. 1988. Rusek, J., New Decomposition Catalysts And Characterization Techniques For Rocket-Grade Hydrogen Peroxide J. of Propulsion and Power, 1996, 12, 574-579. A document entitled Advanced Chemical Propulsion Systems dated Nov. 21, 1995. Berezovsky, Pyrogen Fire Suppression System-Marine & Vehicle Applications dated Aug. 1997. Thomas, Martin, Fire Research News 20.

\* cited by examiner

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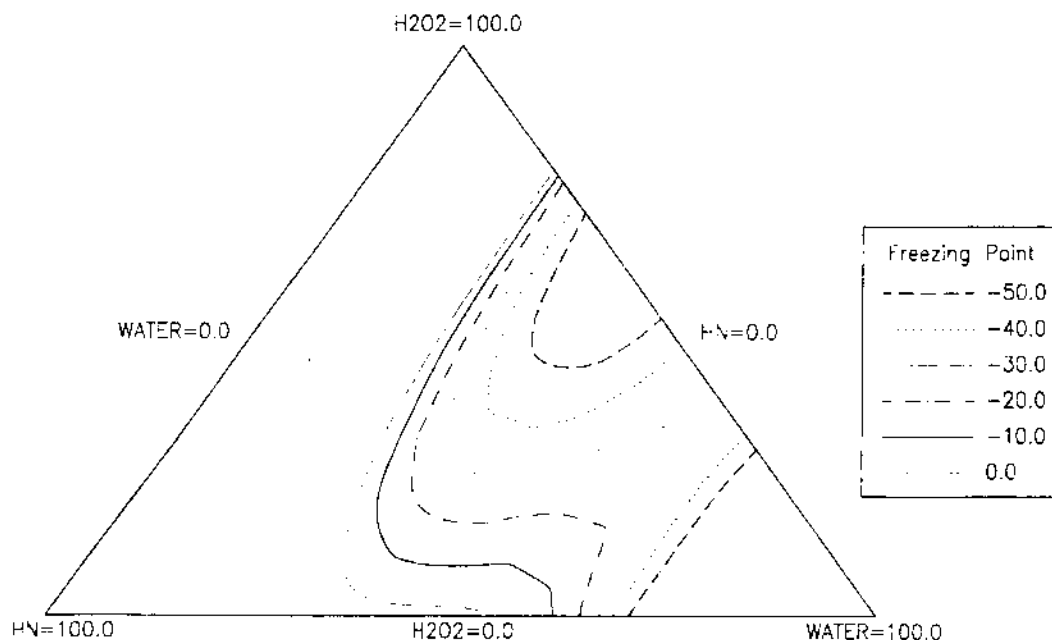
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(57) **ABSTRACT**

A family of water-based gas-generating liquid compositions is described. A composition of the present invention includes: hydrogen peroxide; hydrazinium mononitrate; and water. Compositions of the present invention may be mixed with fuels to make monopropellants or used in bipropellant or hybrid systems. Alternative uses of the present invention include breathable gas generation.

**22 Claims, 2 Drawing Sheets**

**Freezing Points for PERSOL 2 Formulations**



Densities of PERSOL 2 Formulations

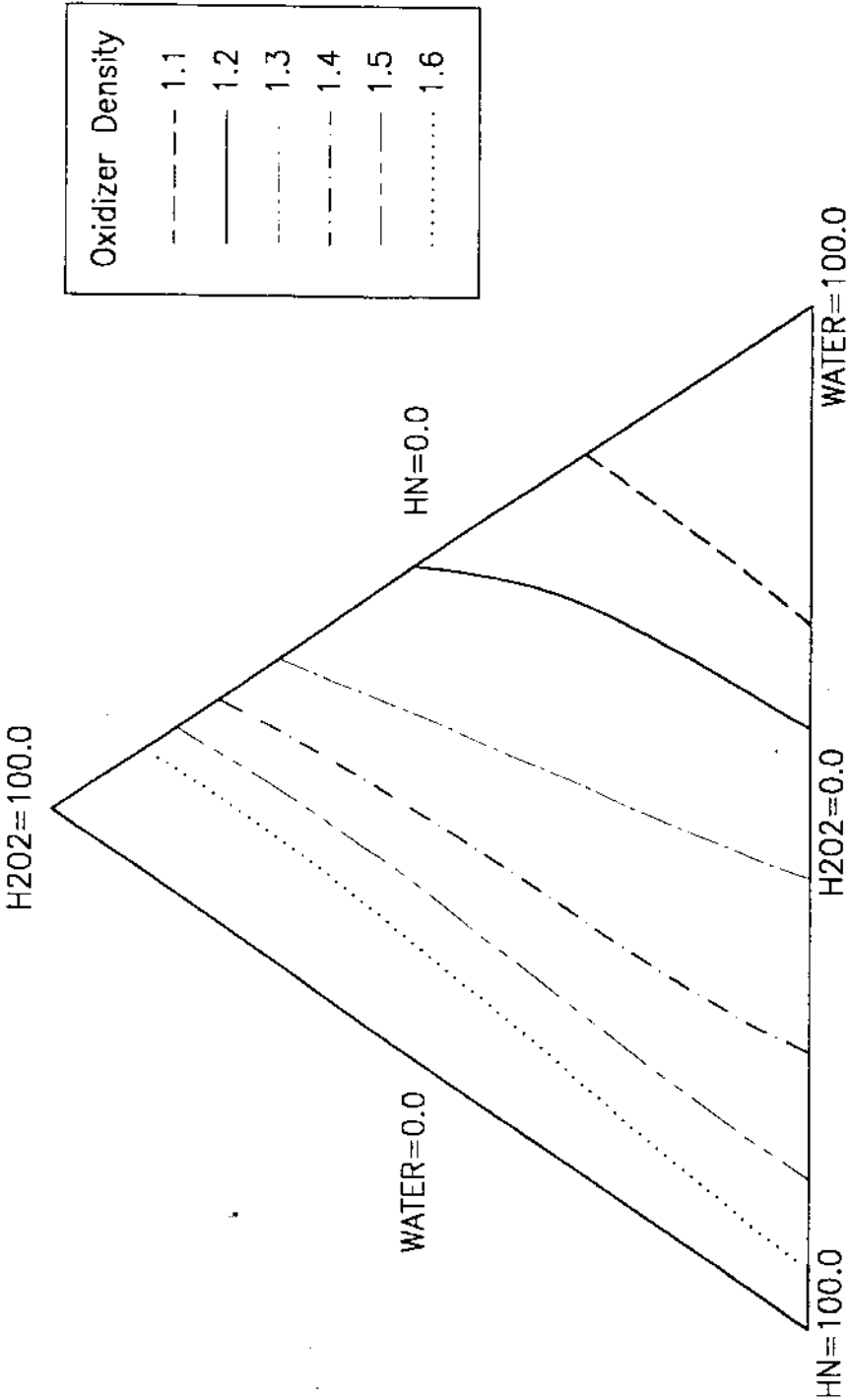


FIG-2

(PyroGen) which is pyrotechnic-driven. The system produces an aerosol, and the composition of the system is not disclosed.

Based on my reading of the contemporary art, I have decided that what is needed is a gas-generating liquid composition which can be used as an oxidizer, and which has low cost, low toxicity and excellent handling properties.

#### SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide improved gas-generating liquid compositions.

It is also an object of the invention to provide improved liquid oxidizers for use in monopropellant and bipropellant systems.

It is another object of the invention to provide improved liquid compositions for generation of breathable air.

It is yet another object of the invention to provide gas-generating liquid compositions which have low cost.

It is still another object to provide gas-generating liquid compositions from readily available components.

It is a further object to provide gas-generating liquid compositions which have low vapor and skin toxicity.

It is a yet further object to provide gas-generating liquid compositions which have a low explosion hazard.

It is a yet still further object to provide compositions having excellent handling and storage characteristics, such as low corrosivity.

It is an additional object to provide gas-generating liquid compositions which are easy to prepare.

It is a yet additional object to provide gas-generating liquid compositions allowing ready production of customized formulations.

It is a still additional object of the invention to provide a gas-generating liquid having a low freezing point.

It is yet another object of the invention to provide a gas-generating liquid which has high density and high energy density.

It is yet another object of the invention to provide a gas-generating liquid which is "green", that is, disposable without damage to the environment.

It is still another object of the invention to provide a gas-generating liquid which allows water-based cleanup of spills.

These objects are achieved in the present invention which provides a family of water-based gas-generating liquid compositions which may be used in rocket propulsion, torpedo propellants, air bags, and other applications. Applications also include use in oxygen generators and in fuel cells.

The general composition of the water-based gas-generating liquid of the present invention includes: hydrogen peroxide; hydrazinium mononitrate (HN<sub>3</sub>) and water. Generally, the water concentration (that is, content) in the gas-generating liquid will be in the range of approximately 15 to 45 percent by weight (w/w-%), and the water concentration may be in the range of 20 to 35 w/w-%. Generally, the hydrazinium mononitrate concentration will be in the range of approximately 25 to 60 w/w-%, and may be in the range of approximately 35 to 60 w/w-%. The concentration of hydrogen peroxide will generally be in the range of approximately 12 to 70 w/w-% and may be in the range of approximately 25 to 50 w/w-%. The gas-generating liquid composition of the present invention may have additional components, such as a colorant, an odorant, a gelant, a thixotropic agent, a surfactant, or a burning rate modifier.

In one embodiment, the gas-generating liquid compositions of the present invention may be added to a fuel to form a monopropellant. In another embodiment of the present invention, the gas-generating liquid composition may consist essentially of hydrogen peroxide, hydrazinium mononitrate and water. Here, "consists essentially of" means that this composition has no added fuel, nor other component substantially affecting the energy content, freezing point, or density of the composition. Such a composition may have minor additional components, such as a colorant, an odorant, a gelant, a thixotropic agent, a surfactant, or a burning rate modifier, which do not substantially affect these parameters.

In addition to the compositions of the present invention, the invention also includes methods of use of the compositions. Specifically, the compositions of the present invention can be used for generating gas by passing the compositions through a solid catalyst bed, heating the compositions, or adding catalyst to the compositions. The compositions can also be mixed with a fuel to form monopropellants or can be used in bipropellant and hybrid rocket systems.

#### BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention, and many of the attendant advantages, thereof, will be readily apparent as the same becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings in which like reference symbols indicate the same or similar components, wherein:

FIG. 1 is a response surface diagram illustrating freezing points of compositions of the present invention; and

FIG. 2 is a response surface diagram illustrating densities of compositions of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The gas-generating liquid compositions of the present invention are a family of compositions which the inventor refers to as PERSOL 2. The general composition of the water-based gas-generating liquid of the present invention includes: hydrogen peroxide; hydrazinium mononitrate; and water. The invention may also comprise any of a number of additives, and may comprise a fuel.

The present invention includes a family of compositions with varying amounts of hydrogen peroxide, hydrazinium mononitrate and water. Preparation of the compositions of the present invention can generally be achieved simply by the mixing the ingredients of the invention. Generally, the water concentration (that is, content) in the gas-generating liquid will be in the range of approximately 15 to 45 percent by weight (w/w-%), and the water concentration may be in the range of 20 to 35 w/w-%. Generally, the hydrazinium mononitrate concentration will be in the range of approximately 25 to 60 w/w-%, and may be in the range of approximately 35 to 60 w/w-%. The hydrogen peroxide will generally be in the range of approximately 12 to 70 w/w-% and may be in the range of approximately 25 to 50 w/w-%. Different compositions will have different values of parameters relevant to the use of the invention, and thus customized compositions of the present invention may be prepared.

Among the advantages of the present invention are the low freezing point achievable in some compositions. An important parameter of liquid gas-generating compositions is the freezing point. At temperatures below the freezing point, solids appear in the liquid, affecting many aspects of

Another advantage of the present invention is the customizability of the formulation. In particular, by adjusting the water content of the final formulation, the combustion temperature can be adjusted to give a desired flame temperature or to achieve specific physical/chemical/safety properties. For example, this can reduce the vulnerability characteristics and the corrosivity/erosion problems associated with the exhaust gases.

Another advantage of the present invention is cost. Hydrogen peroxide, in particular, is relatively inexpensive.

In addition to the hydrogen peroxide, hydrazinium mononitrate and water, compositions of the present invention may also contain additives to modify other properties of the gas-generating liquids. These additives usually total less than 1 percent by weight of the composition. For example, the composition may contain a colorant. This is a dye which allows the gas-generating liquid to be more easily seen. This is particularly useful, for example, in locating spills.

Another additive which may be used is an odorant. This is a compound with an odor readily detected by the human nose, and is generally used for detecting and locating spills.

Another additive which may be used is a stabilizer. This will usually be an oxygen scavenger, such as ammonium thiosulfate, which serves to slow chemical degradation of the gas-generating liquid.

Another additive which may be used is a chelating agent, such as ethylenediamine tetraacetic acid (EDTA) or cyclohexanediaminetetraacetic acid (CDTA) or sodium salts of these compounds. Chelating agents serve to bind impurity metal ions in the liquid, and can serve to slow degradation of the gas-generating liquid.

Another additive which may be used is a gelant, or gelling agent. Having the gas-generating liquid in gel form may be useful in certain applications.

Another additive which may be used is a thixotropic agent. Such an agent can improve the general handling properties of the liquid, such as pumping or pouring.

Another additive which may be used is a burning rate modifier. Such an additive affects the kinetics, or rate of burn of compositions.

Another additive which may be used is a surfactant. Surfactants can serve to allow miscibility of the gas-generating liquid with certain fuels. Also, a surfactant can serve to modify the droplet size of the gas-generating liquid when it is sprayed, for example into a rocket combustion chamber.

The compositions of the present invention may be used as liquid oxidizers for a variety of propellant systems. In general, propellant systems are monopropellant or bipropellant systems.

In theory, a liquid monopropellant is the ideal energy source for various liquid gas generator applications such as gun propellants, air bag inflators, torpedo propulsion and rocket motors. The monopropellant's main advantage is simplicity when compared to liquid bipropellant systems; a monopropellant requires only half the number of pumps, valves, storage tanks and pipes. An example of a monopropellant is the nitrate ester-based Otto fuel used in torpedoes.

When used as a monopropellant, a composition of the present invention would generally be preblended with a fuel. Such a fuel could be a water-soluble fuel, in which case the fuel would generally dissolve in the liquid oxidizer. Non-water soluble fuels, such as hydrocarbons, may also be used. Monopropellants using hydrocarbons and the liquid oxidizers of the present invention would generally be emulsified

mixtures. In some cases, surfactants may be added to allow for better emulsification. Among the fuels that may be used with the invention are alkylammonium nitrates and alkanolammonium nitrates having one, two or three carbon atoms.

Monopropellants made using the liquid oxidizer of the present invention may be used for other purposes. If the oxidizer containing hydrogen peroxide, ammonium nitrate and water is mixed in appropriate ratio with a fuel, for example urea, an alkylammonium nitrate or hydrocarbon, the decomposition reaction can in theory yield nitrogen, carbon dioxide, carbon monoxide and water. Such a decomposition mixture would not support combustion, and might be usable in air-bag inflation, fire suppressant or related uses.

In practice, most liquid propellant systems use bipropellants. One problem with some liquid monopropellants is the low energy content of the monopropellant, in order to meet physical, chemical and safety requirements. If the oxidizer and fuel are separated, the sensitivity to shock, friction and static discharge are reduced. The homogeneous mixture of the two components of a liquid propellant has a sensitivity which is greater than that of either component.

Bipropellant systems are commonly used in rocket motors. In a bipropellant system, the liquid oxidizer contacts the fuel at the time of combustion. Rocket motors may use liquid fuel, or in the case of hybrid rocket motors, the fuel may be solid. The compositions of the present invention may be usable as liquid oxidizers for both kinds of rocket motors. Metallic additives may be added to these fuels to improve the propellants' energy outputs.

In general, catalytic or thermal combustion of an oxidizer composition of the present invention with a low-carbon content fuel should generate an exhaust gas containing  $N_2$ ,  $H_2O$ , and some  $CO_2$ . Catalytic or thermal combustion of an oxidizer composition of the present invention should generate an exhaust gas containing  $N_2$ ,  $H_2O$ ,  $CO_2$ ,  $CO$ ,  $CH_4$  and other gases. However, no HCN is expected in the exhaust gas, unlike exhaust gases resulting from nitrate ester fuels.

The compositions of the present invention may also be decomposed to yield gases and energy. This decomposition may be achieved by catalysis. For example, placing the composition of the present invention in contact with a fixed bed catalyst, such as Pt, Pd, or  $MnO_2$ , may yield decomposition. Such a reaction is well known in the art for other liquids, for example, hydrogen peroxide decomposing to water and oxygen. Alternatively, the composition of the present invention might be decomposed by adding a catalyst to the composition to dissolve or suspend the catalyst. This may be done in a catalyst stream flow process. For example, the composition of the present invention and a catalyst could be delivered from a bladder and mixed upon delivery, by methods known in the art.

Alternatively, decomposition of a composition of the present invention may be achievable by heating the composition. If, for example, the composition is injected into a hot reaction chamber, the heat of decomposition may be sufficient to self-sustain the decomposition reaction, and a continuous decomposition of a stream of the composition may be possible.

One possible application of decomposition of compositions of the present invention is in breathable air generators. Hydrazinium nitrate and hydrogen peroxide may be theoretically decomposed to oxygen, nitrogen and water according to the following stoichiometries:

